Valorization Of Bioglycerol Through Dehydration Followed By Electrochemical Conversion

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Abstract: In this study, electrochemical valorization of glycerol was conducted in a two-compartment electrolysis cell. This novel method consisted of two steps; glycerol was first treated by concentrated sulphuric acid for dehydration to favour the electron transfer then was subjected to electrolysis. The glycerol conversion in the dehydration process was optimized using the Design of Experiment (DOE) methodology by studying the effect of reaction temperature, reaction time and mole ratio acid to glycerol. During the glycerol dehydration and electrochemical process, various high potential added-value compounds were produced such as glycerol acetal, glycerol ether and diethyl succinate. The possible reaction mechanisms for the formation of these added-value chemicals are also proposed.

Introduction

Bioglycerol is the main by-product generated from biodiesel production, with approximately 10 % wt of the total product. In addition, during oleochemical production bioglycerol is largely produced as by-product in oil hydrolysis process [1]. At present, two-third of the world glycerol supply is produced from biodiesel and oleochemical industries [2]. The current market value of bioglycerol is at its minimum due to its oversupply. Therefore, it is necessary to find alternative applications for bioglycerol. Today, a lot of research is devoted to transform bioglycerol into various high added-value chemicals such as 1,3-propanediol, acrolein, glycerol acetal, glycerol ether, ethylene glycol, glycerol carbonate, 1,2-propanediol, dihydroxyacetone (DHA), etc.[3-7].

Previous works have shown that a number of selective processes can be used to convert bioglycerol into wide variety of added-value compounds, for instance selective oxidation, etherification, hydrogenolysis, catalytic reforming, dehydration and fermentation. During biofermentation process, expensive equipment and biocatalyst such as *Klebsiella pneumonia*, *Clostridium butyricum*, *Citrobacter freundii*, *Lactobacillus reuteri*, *Halonaerobium saccharolyticum* are involved to convert glycerol into 1,3-propanediol [8, 9]. In chemical catalytic process, Abbadi *et al.* reported that glycerol can be oxidized into oxalic acid via bismuth-modified platinum catalyst [10]. Another selective oxidation process was done by Kimura *et al.*, to convert the glycerol into tartronic acid using CeO_2 supported on Pt as catalyst [11]. Many studies on glycerol hydrogenolysis via heterogeneous or homogeneous catalytic methods were also described to reform glycerol into 1,2-propanediol, 1,3-propanediol and ethylene glycol [12, 13]. However, these processes have many drawbacks, such as low selectivity and yield. Besides, some of them may require high running production cost, high pressure and high temperature are applied during the process [9, 14]. Those drawbacks may have negative impacts to the environment and basically they are not economically practical.

In order to address these shortcomings of the existing methods, electrochemical methods are introduced. From the studies done by Gomes *et al* and Kwon *et al*, during the glycerol electrooxidation reaction, the following products were formed: glycolate, glycoxylate, tartronate, carbonate and formate [15, 16]. Simões *et al.* were the first authors to discuss the electrochemical oxidation of glycerol for cogenerating energy with other added-value chemicals [17, 18]. Zhang *et al.* also did a similar study as Simões *et al.* with using Pt/C as anode catalyst and Fe-Cu-N_4/C as cathode catalyst. They found that the glycerol electrooxidation has a very high selectivity in glyceric and tartronic acids [16, 19]. Based on the previous studies, much attention was being paid on the electrooxidation of glycerol, yet lack of relevant information regarding on the study for the whole process of electrooxidation and electroreduction of glycerol.

In this study, a novel method is adopted, to convert bioglycerol via electrochemical method over concentrated acidic medium in a two-compartment electrolysis cell separated by ceramic porous cup. This simple and robust synthesis route consists of two reaction steps. During the first step, glycerol is dehydrated over acidic medium in order to prior to electron transfer. In the second step, electricity is applied. In this article, the possible compounds that formed during the dehydration and electrochemical process in the cathodic and anodic regions are identified and the reaction mechanisms are proposed.

Results and Discussion

Preliminary Experiment: Cyclic Voltammetry

Before starting the trials, the possible electrochemical conversion of glycerol was confirmed by cyclic voltammetry (CV) technique. A typical CV curve of 10 ml H_2SO_4 (0.1 M) and 10 ml glycerol aqueous solution (0.3 M), with an applied potential of +2.00 to -0.50 V is shown in **Figure 1**. During the cathodic scan, the current increased at a potential above -0.24 V, which indicates the reduction of H^+ to H_2 (region A). Besides another reductive peak was observed at +0.35 V (peak I) which is attributed to the reduction of Pt-oxide [20] as below:

$$PtO + H^+ + e^- \rightleftharpoons PtOH \qquad \text{(Eq. 1)}$$

In the anodic scan, the oxidation of H_2O to O_2 (region B) was observed at potential above +1.35 V. With the presence of glycerol, another two oxidation peaks were observed at +0.60 V (peak II) and +0.75 V (peak III) which are assigned to the oxidation of glycerol [21, 22].

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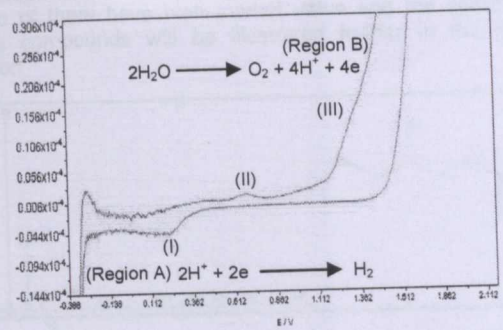


Figure 1. Cyclic voltammetry curve of glycerol aqueous solution in acidic medium over Pt working electrode at a scan rate of 5 mVs^{-1} with an Ag/AgCl reference electrode

Optimization: ANOVA Model

The optimization study of glycerol dehydration was carried out by DOE software. The relation between the response factor (glycerol conversion) and three operating variables (reaction time, reaction temperature and mole ratio of acid to glycerol) was mathematically modelled by RSM based on the **Eq. 4**. The model in terms of actual factors is shown in the following equation:

$$Ract = +\ 99.40900 + 0.019037A + 0.77941B - 0.031206C - (1.58793E\text{-}004)A^2 - 0.27172B^2 + (2.33653E\text{-}004)C^2 - (3.73620E\text{-}004)AB + (8.90415E\text{-}006)AC + (2.26866E\text{-}003)BC \quad \textbf{(Eq. 2)}$$

Where, *Ract* is the glycerol conversion, *A* is the reaction time, *B* is the mole ratio of acid to glycerol and *C* is the reaction temperature.

The data obtained from ANOVA validates that this model was significant, with the P-Value less than 0.05. **Figure 2 (a), (b)** and **(c)** display the 3D-RSM plots for glycerol conversion at different reaction times and mole ratios (H_2SO_4:Glycerol) under constant reaction temperatures at 40 °C, 60 °C and 80 °C, respectively. The maximum conversion of glycerol was obtained at 60 min reaction time. As expected, the results showed that the concentration of H2SO4 is an important parameter. At low H_2SO_4 concentrations the conversions were low. . The optimum operating conditions predicted by the ANOVA model are 80 °C (reaction temperature), 60 min (reaction time) and mole ratio (H_2SO_4:Glycerol) at 2:1. In order to allow the glycerol to react completely, excess of H_2SO_4 is desirable. This optimum condition was applied to the electrochemical system. The best glycerol conversion obtained is 99.8 %. Generally, the glycerol conversions from previous published works are around 15 - 86 % [13, 14], which were relatively low as compared to this process. In this study, the concentrated sulphuric acid might has acted as an excellent dehydrating agent to help to eliminate one or more hydroxyl group from glycerol [23].

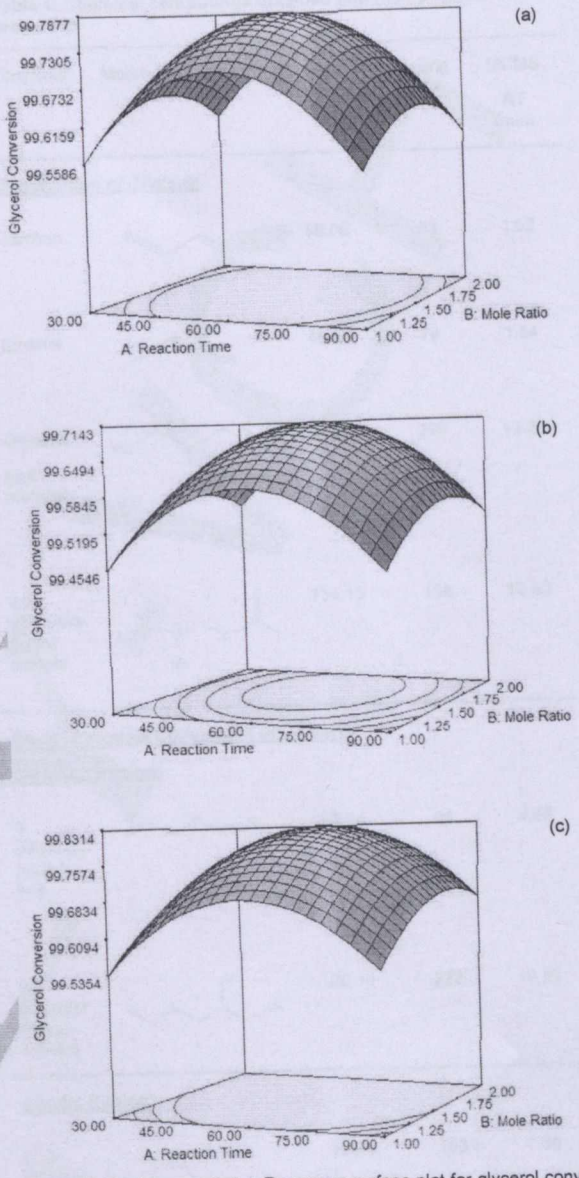


Figure 2. Design-expert plot: Response surface plot for glycerol conversion at different mole ratio and reaction time; (a) at reaction temperature 40 °C, (b) at reaction temperature 60 °C and (c) at reaction temperature 80 °C

Products Identification and Reaction Mechanisms

The products generated during the dehydration and electrochemical processes were identified by GC-MS. The characteristics of these compounds were determined by matching with the existing GC-MS library software. From the GC-MS spectra shown in **Figure 3**, several chemical compounds were obtained from the dehydration process, such as unreacted glycerol, acrolein, ethanol and 2,3-dihydroxypropyl acetate. On the other hand, after electrolysis, two chemical compounds were observed in the cathodic region, namely 3-(allyloxy)-prop-1-ene and 3-ethoxypropane-1,2-diol (**Figure 4**). Whereas, in anodic region, chemical compounds such as (1,3-dioxolan-4-yl)-methanol, 1,3-dioxan-5-ol and diethyl succinate were detected (**Figure 5**). The retention times and physical

properties of these compounds are summarized in **Table 1**. Some of them have high market value and the application of these compounds will be illustrated further in the following section.

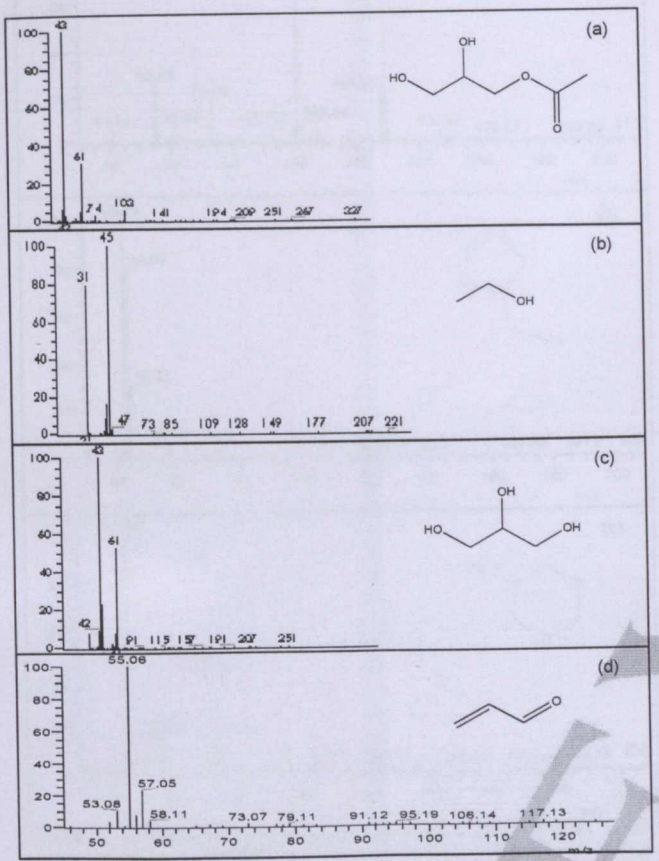


Figure 3. GC-MS spectra of chemical compounds obtained from dehydration of glycerol; (a) 2,3-dihydroxypropyl acetate, (b) ethanol, (c) glycerol, and (d) acrolein

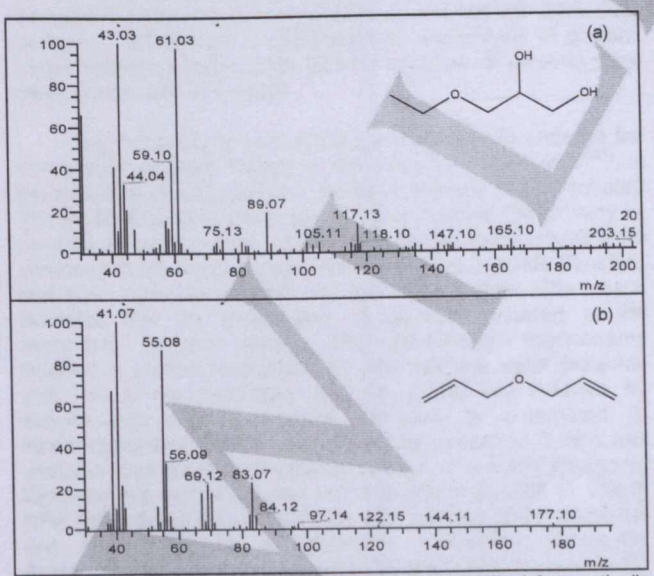


Figure 4. GC-MS spectra of chemical compounds obtained from cathodic region; (a) 3-ethoxypropane-1,2-diol and (b) 3-(allyloxy)-prop-1-ene

Table 1: Chemical compounds obtained and their physical properties

Chemical	Molecular Formula	MW ($g.mol^{-1}$)	Boiling Point (°C)	GCMS RT (min)
Dehydration of Glycerol				
Acrolein		56.06	53	1.62
Ethanol		46.07	78	1.54
Glycerol (raw material)		92.09	290	13.28
2,3-dihydroxy propyl acetate		134.13	158	13.80
Electrochemical Conversion of Glycerol				
Cathodic Region:				
3-(allyloxy)-prop-1-ene		98.14	94	4.69
3-ethoxypropane-1,2-diol		120.15	222	10.53
Anodic Region:				
(1,3-dioxolan-4-yl)-methanol		104.1	193	7.60
1,3-dioxan-5-ol		104.1	193	8.02
diethyl succinate		174.19	217	15.66

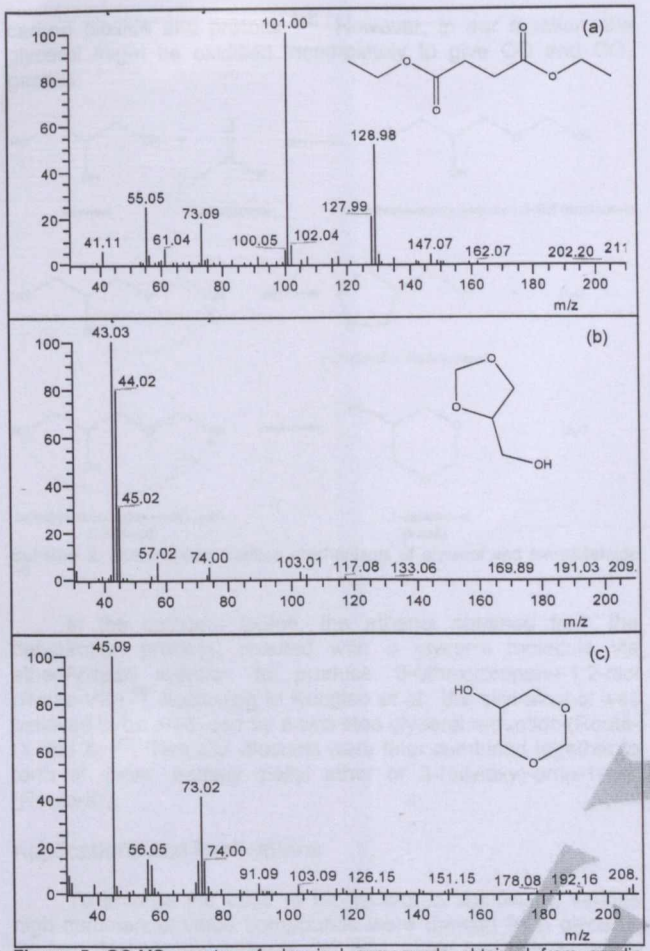
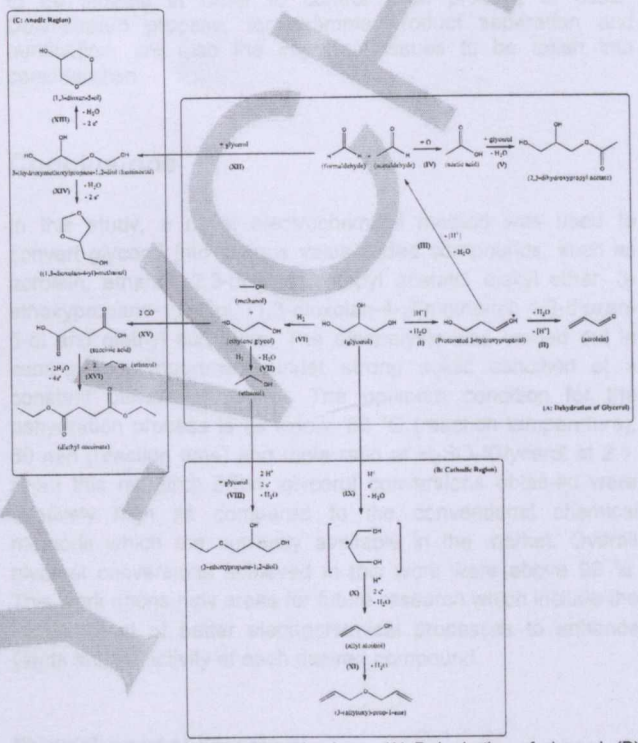


Figure 5. GC-MS spectra of chemical compounds obtained from anodic region; (a) diethyl succinate, (b) (1,3-dioxolan-4-yl)-methanol and (c) 1,3-dioxan-5-ol

The possible reaction mechanisms are proposed in **Scheme 1**. In this study, the reaction is classified into three main pathways; dehydration and followed by electrolysis of glycerol where electro-oxidation and electro-reduction of glycerol were taken part in different region.

Before electricity was applied, glycerol would undergo the dehydration process. Based on the study by Nimlos *et al.*[24], in the presence of acid, glycerol can be protonated and dehydrated. The protonation of glycerol can happen at either the primary or secondary hydroxyl group. Three dehydration mechanisms were proposed in his study; pinacol rearrangement (hydride transfer), pericyclic dehydration and substitution reaction. Our result indicates that the protonation of glycerol occurred at the secondary hydroxyl group. The dehydration mechanisms involved is pinacol rearrangement whereby one water molecule was lost at the secondary hydroxyl group and followed by simultaneous hydride transfer to form of protonated 3-hydroxylpropanal (3-HPA) (Route-I). The generated 3-HPA was unstable and readily dehydrated further to acrolein (Route-II), therefore this compound was not detected in GC-MS [5]. The 3-HPA did undergo 1,2-dehydration with the loss of formaldehyde and contributed to acetaldehyde production (Route-III). Acetaldehyde continuously oxidized to acetic acid in route IV [25], which subsequently reacted with glycerol to form 2,3-dihydroxypropyl acetate (Route-V). On top of that, glycerol also went through the hydrogenolysis process via cleavage of the C-C bond and leading to the formation of methanol and ethylene glycol (Route-VI), and further dehydrated to ethanol (Route-VII) [12].



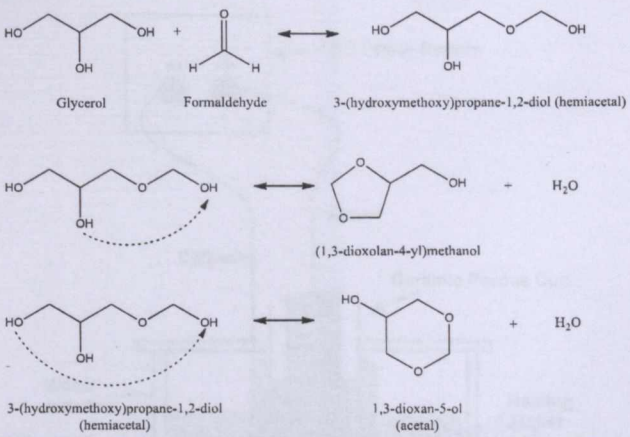
Scheme 1. Proposed reaction mechanisms. (A) Dehydration of glycerol, (B) Electro-reduction of glycerol (cathodic region) and (C) Electro-oxidation of glycerol (anodic region)

In the presence of electricity; acid, glycerol and other intermediates obtained after the dehydration process, can be directly oxidized or reduced in the anodic and cathodic compartments, respectively. In the anodic region, formaldehyde obtained earlier in the dehydration process was quite reactive and readily reacted with glycerol via acetalization to form of 3-(hydroxymethoxy)propane-1,2-diol (Route-XII). Based on the case study by Agirre and his co-workers [4], they have implemented the reaction mechanisms that were reported by Chopade and Sharma [26]. Here, the glycerol first reacted with formaldehyde to form of hemiacetal (3-(hydroxymethoxy)propane-1,2-diol), and secondly the two hydroxyl group of hemiacetal joined together to form dioxolane as shown in **Scheme 2**. In this case, the hemiacetal molecule reorganized to yield (1,3-dioxolan-4-yl)-methanol (Route-XIV) and 1,3-dioxan-5-ol (Route-XIII), respectively. On the other hand, the generated ethylene glycol from dehydration process was carbonilized by CO to form succinic acid (Route-XV), which subsequently reacts with two molecules of ethanol to form diethyl succinate (Route-XVI). The CO that observed in the anodic region was possibly come from the following electro-oxidation of glycerol:

$$C_3H_8O_3 + H_2O \longrightarrow CO_2 + 2\,CO + 10\,H^+ + 10\,e^- \quad \textbf{(Eq. 3)}$$

Based on the review article published by Simões *et al.*, in the anodic region, glycerol can be electro-oxidised completely to

carbon dioxide and protons [18]. However, in our reaction, the glycerol might be oxidised incompletely to give CO and CO_2 gasses.



Scheme 2. Acetalization reaction mechanisms of glycerol and formaldehyde [28]

In the cathodic region, the ethanol obtained from the dehydration process, reacted with a glycerol molecule via etherification reaction to produce 3-ethoxypropane-1,2-diol (Route-VIII) [6]. According to Kongjao *et al.*, the allyl alcohol was believed to be produced by a two-step glycerol reduction (Route-IX and X) [21]. Two allyl alcohols were later combined together to form of dimer, namely diallyl ether or 3-(allyloxy)-prop-1-ene (Route-XI).

Applications and Implications

To enlarge the uses of bioglycerol in worldwide, various high commercial value compounds were derived from glycerol. During the electrosynthesis in this study, a few potential chemicals were obtained from glycerol conversion, such as glycerol acetal: (1,3-dioxolan-4-yl)-methanol and 1,3-dioxan-5-ol, glycerol ether: 3-ethoxypropane-1,2-diol, and succinic acid derivative: diethyl succinate.

The glycerol mono-ether that was obtained in this study can be seen as an interesting intermediate for the production of glycerol acetals e.g. dioxolane and dioxane, which have numerous applications in the current market. From the previous studies, glycerol acetals are mainly used in pharmaceutical industries, cosmetics and fragrances, food industries, flavors, surfactants and disinfectants [7, 27]. In this study, similar types of glycerol acetals were produced as in Agirre (2011), which can be used as additives for biodiesel or diesel to replace the widely used metal based additives which have bad impact on the environment during the biodiesel or diesel combustion [4]. Another green chemical, succinic acid derivative, that obtained can replace the petroleum-based maleic anhydride to produce 3-hydroxypropionic acid, γ-butyrolactone, 1,4-butanediol, tetrahydrofuran and polymers via hydrogenation process [28]. These chemicals are used as intermediate chemicals and solvent for the pharmaceutical, textile and food industries [29].

In this article, only glycerol conversion is reported however the percentage of yield of each compound obtained is not reviewed as optimization studies are still under progress. Based on the reaction mechanisms proposed, in order to increase the selectivity, effect of applied current and acid concentration are the main factors to be concerned. Another great challenge to overcome of this process is the electro-oxidation of glycerol as in **Eq. 3** to form of CO and CO_2 gasses, as well as cleavage of glycerol C-C bond to give smaller molecule instead of deriving useful molecule from glycerol. Temperature is a key parameter to be studied in order to control such process to occur. Downstream process, for example product separation and purification, are also the important issues to be taken into consideration.

Conclusions

In this study, a novel electrochemical method was used to convert glycerol into various value-added compounds, such as acrolein, ethanol, 2,3-dihydroxypropyl acetate, diallyl ether, 3-ethoxypropane-1,2-diol, (1,3-dioxolan-4-yl)methanol, 1,3-dioxan-5-ol and diethyl succinate. The electrolysis was carried out in separating compartment under strong acidic condition at a constant current of 1.4 A. The optimum condition for the dehydration process is as follow: 80 °C (reaction temperature), 60 min (reaction time) and mole ratio of H_2SO_4/Glycerol at 2:1. From this research effort, glycerol conversions obtained were relatively high as compared to the conventional chemical methods which are currently available in the market. Overall glycerol conversions achieved in this work were above 99 %. This work opens new areas for future research which include the development of better electrochemical processes to enhance yields and selectivity of each desired compound.

Experimental Section

Materials

Reagent grade glycerol (99.5 %, v/v) and analytical grade sulphuric acid (98.0 %, v/v) were supplied by Fisher Scientific, Malaysia.

Cyclic Voltammetry

The possible electrochemical reforming of glycerol in acidic medium was explored using cyclic voltammetry (CV) with a Potentiostat/Galvanostat (Autolab, model PGSTAT20). Pt planar (total surface area of 0.017 cm^2) and Pt rod were used as the working and counter electrodes, respectively, while Ag/AgCl was used as the reference electrode. The scan potential was varied in the range +2.00 to -0.50 V at a scan rate of 5 $mV.s^{-1}$, and the system was agitated at 350 rpm.

Dehydration and Electrochemical Reaction

Glycerol dehydration process was performed in a cylindrical reactor with the presence of concentrated sulphuric acid, H_2SO_4 (18 M). The reaction temperature was controlled by a heating jacket; a magnetic bar was used to stir the mixture at 350 rpm. Various factors such as reaction temperature (40-80 °C), reaction time (30-90 min) and mole ratios of acid to glycerol (1, 1.5 and 2) were studied.

The electrochemical reaction was carried out by applying the external electricity directly towards the reaction mixture obtained from dehydration process. In the same cylindrical reactor, the solution was separated by a cylindrical ceramic porous cup (<0.5 μm) into two compartments, cathodic and anodic regions, respectively (**Figure 6**). External electricity was supplied by a regulated DC power supply at a constant current of 1.4 A. Two platinum (Pt) meshes electrodes in a cylindrical and rectangular shape, with total surface area of

approximately 44 cm^2 and 6 cm^2 were used as the cathode and anode, respectively.

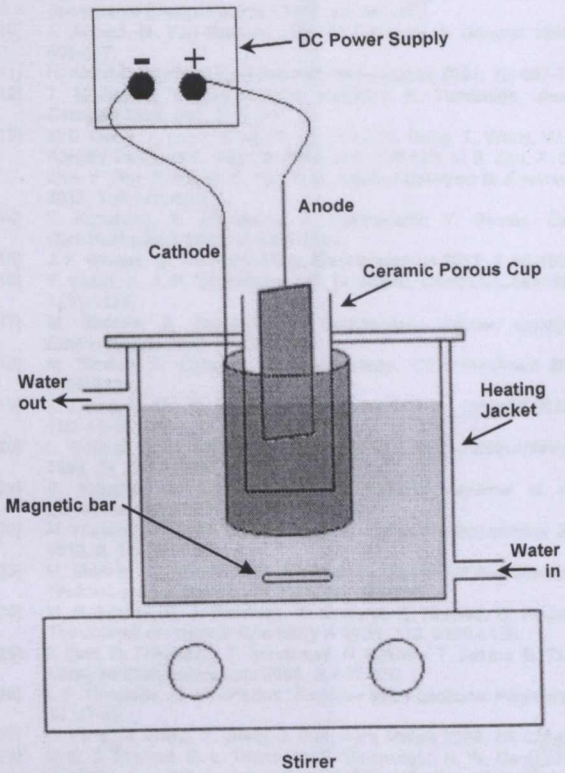


Figure 6. Experimental set-up for electrochemical reforming of glycerol

Experimental Design and Optimization

The statistical design of experiment and optimization studies was carried out with the Design-Expert Software (DOE). Central composite design (CCD) and response surface methodology (RSM) were applied to optimize the three operation variables; reaction temperature (°C), reaction time (min) and mole ratio of acid to glycerol. Glycerol conversion (%) was used as response factor for the study. In this design, 17 experiment trials including 3 centre point runs were set at 3 variables levels. The optimum conditions can be expressed by the following second order polynomial quadratic equation at three independent variables:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_1 X_1^2 + \beta_2 X_2^2 + \beta_3 X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + e \quad \textbf{(Eq. 4)}$$

Where, β is the regression coefficient and e is the random error.

The competency of this model was diagnosed from the statistical results provided in the analysis of variance (ANOVA). Statistical significance was checked by the P-value. Three dimensional (3D) RSM plot was obtained from the function from **Eq. 4**.

Analysis

The chemical compounds generated in dehydration and electrochemical processes were analysed by Gas Chromatography-Mass Spectroscopy (GC-MS) (Model Thermo Finnigan & Polaris Q, Thermo Finnigan). Samples were firstly diluted with ethanol at 10 ppm. Internal standard, ethyl acetate, was added into each sample for reference. Finally, the diluted samples were neutralised with sodium hydroxide (NaOH) before they were injected into GC-MS. The GC-MS analysis conditions are shown in **Table 2**. Headspace GC-MS analysis was used to analyse the volatile compounds. In this analysis, sample was dissolved in water and vaporised into gaseous phase before injection. The glycerol conversion was quantified by Gas Chromatography (GC) (Model 6890, Agilent). The sample preparation is similar to GC-MS analysis and the analysis conditions are presented in **Table 3**.

Table 2. Gas chromatography mass spectroscopy analysis conditions

Instrument	Trace GC, Thermo Finnigan & Polaris Q, Thermo Finnigan
Column	ZB-5 MS (30 m x 0.25 mm x 0.25 µm)
Detector	MS
Carrier Gas	He
Injector Temperature	250°C
Flow Rate	1 $ml.min^{-1}$
Injection volume	1 µl
Oven Temperature	45°C (5 min) → 7°$C.min^{-1}$ → 150°C → 15°$C.min^{-1}$ → 310°C
Ionisation	Electron impact (70eV)

Table 3. Gas chromatography analysis conditions

Instrument	Agilent, Model 6890
Column	HP-5 (30 m x 0.25 mm x 0.25 µm)
Detector	FID
Carrier Gas	He
Injector Temperature	250°C
Detector Temperature	250°C
Flow Rate	8 $ml.min^{-1}$
Injection volume	1 µl
Oven Temperature	60°C (2 min) → 7°$C.min^{-1}$ → 150°C → 15°$C.min^{-1}$ → 310°C

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Keywords: Bioglycerol • Dehydration • Biodiesel • Electro-oxidation • Electro-reduction

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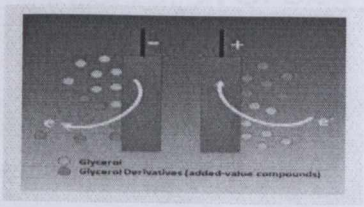

Figuring out the chemistry behaviour: Glycerol can be diversified into various chemical compounds through electrochemistry. In this article, the chemistry behaviour of glycerol in electrochemistry is proposed.

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